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**SYNTHESIS OF LOW TEMPERATURE
OIL RESISTANT URETHANE
ELASTOMERS**

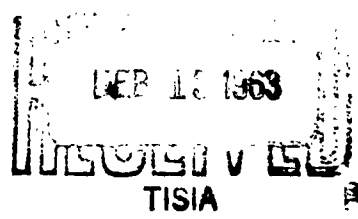
QUARTERLY PROGRESS REPORT No. 2

1 January 1963

FOR

**ROCK ISLAND ARSENAL
ROCK ISLAND, ILLINOIS**

CONTRACT No. DA-20-018-ORD-24883



**WYANDOTTE CHEMICALS CORPORATION
WYANDOTTE, MICHIGAN**

Wyandotte Chemicals Corporation

wyandotte • michigan

January 31, 1963

Subject: Quarterly Progress Report No. 2
Contract No. DA 20-018-ORD-24883

Gentlemen:

This enclosed report is sent to you at the request of Non-Metallic Materials Section, Rock Island Arsenal Laboratories.

Any comment or correspondence concerning the material contained in this report should be directed to:

Commander
Non-Metallic Materials Section
Rock Island Arsenal
Rock Island, Illinois

Yours very truly,

WYANDOTTE CHEMICALS CORPORATION



S. L. Axelrood
Polymer Research Department

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ARMY ORDNANCE CONTRACT NO. DA 20-018-ORD-24883

NON-METALLIC MATERIALS SECTION

ROCK ISLAND ARSENAL LABORATORIES

QUARTERLY PROGRESS REPORT NO. 2

COVERING PERIOD 1 OCTOBER 1962 TO 31 DECEMBER 1962

SYNTHESIS OF LOW TEMPERATURE

OIL RESISTANT URETHANE ELASTOMERS

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WYANDOTTE CHEMICALS CORPORATION

WYANDOTTE, MICHIGAN

FOREWORD

This report was prepared by the Polymer Research Department, Industrial Chemicals Research Division of Wyandotte Chemicals Corporation, Wyandotte, Michigan under Army Ordnance Contract No. DA-20-018-ORD-24883. This work is being technically administered under the direction of the Non-Metallic Section of the Rock Island Arsenal Laboratories, Rock Island, Illinois with Messrs. R. Shaw and Z. Ossefort acting as Project Engineers.

The personnel of Wyandotte Chemicals Corporation assigned to this project are Messrs. S. Axelrood, Project Leader, and W. Lajiness under the general direction of Drs. E. J. Fujiwara and K. C. Frisch.

This report covers the period 1 October 1962 to 31 December 1962.

ABSTRACT

Preparation and evaluation of urethane-urea elastomers were continued this second quarter. Based on work performed in the first quarter, dichlorobenzidine (DCB) and toluene diisocyanate were the diamine and diisocyanate chosen for the bulk of the work. The amine to hydroxyl ratio was varied on urethane-urea elastomer formulations based on two polyether triols, a 5200 molecular weight polypropylene ether triol and a 7000 molecular weight polyether triol containing a large percentage of ethylene oxide. The amine to hydroxyl ratio was varied from 1.5 to 2.5 in the series based on the former triol, from 1.5 to 10 on the latter triol. There was surprisingly little variation in torsional modulus at -55°C with variations in amine to hydroxyl ratio, even over the range from 1.5 to 10.0/1. However, as the amine to hydroxyl ratio increased from 1.5/1 to 10/1, the room temperature torsional modulus increased from 260 to 3200. Introduction of ethylene oxide into the polyether chain decreases the oil absorption at the expense of increased water absorption.

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INTRODUCTION

There are military needs for materials that are chemical and oil resistant and possess elastomeric properties over a broad range of climatic conditions ranging from that encountered in the tropics to the arctic regions. Many commercial urethane elastomers possess properties which make them serviceable under normal or more prevalent conditions. However, they do not possess the combined properties of low temperature flexibility and oil resistance.

The objective of this program is the development of a urethane elastomer(s) with the following target properties:

- a. Tensile Strength - 1200 psi. Min. (ASTM D412).
- b. Ultimate Elongation - 200% Min. (ASTM D412).
- c. Compression Set, ASTM D395, Method B, after 70 Hrs. at 212°F. - Max. 50%.
- d. Compression Set, ASTM D1229, or Hrs. at -67°C. - Max. 50%.
- e. Oil Swelling, ASTM No. 3 Oil 70 Hrs. at 212°F. - Limits 0 to 10% (ASTM D471).
- f. No cracks, breaks, fissures after testing in accordance with ASTM D746 at -67°F.
- g. Young's Modulus of Elasticity at - 67°F. Max. 10,000 psi. (ASTM D1053).
- h. Uncured and cured elastomers shall be stable for extended periods of storage at ambient temperatures. Little or no change in properties shall be observed after storage for periods up to 2 years. - Max. 10%.
- i. Vulcanizates of the elastomer shall show retention of a minimum of 75% of original tensile and elongation after 70 hours in a circulating air oven at 212°F. (ASTM D573-53).

Although the final elastomer(s) are not limited to the above target properties, the key targets for achievement are (e) and (g).

A review of the properties of urethane elastomers which had previously been developed at Wyandotte, revealed a trend towards improved low temperature flexibility when higher molecular weight polyether polyols were used. Theoretical considerations indicated that if higher molecular weight polyether polyols were to be used, the low temperature flexibility performance could be improved. Oil resistance requirements were met by certain Wyandotte developed polyether elastomers based on lower molecular weight polyether polyols. However, as the polyether molecular weight increased, the oil resistance dropped. A survey of the open urethane literature and data from Wyandotte urethane research revealed that solvent (oil) resistance may be improved by a number of factors, including types of diamine, diisocyanate and polyol used and variations of same. The problem, in view of the above considerations, has been resolved to gaining low temperature flexibility by the use of high molecular weight polyether polyols and investigating which of the factors that improve the solvent (oil) resistance does not appreciably affect the low temperature flexibility.

During the first quarter a statistically designed set of experiments investigating 5 variables at two levels were completed. This investigation was based on the above considerations. Two aromatic diamines (MOCA and DCB) were compared at two levels of amine to hydroxyl ratio. Two aromatic diisocyanates (TDI and MDI) at two levels of concentration were also compared. Two polyols of 1500 equivalent weight were utilized to round out the five variables. These polyols are PLURACOL TP-4542 and Teracol 30. The use of ortho dichlorobenzidine (DCB) at a 1.5 NH_2/OH ratio in combination with tolylene diisocyanate and the polypropylene-ethylene ether triol came the closest to meeting the Army specification for an oil resistant rubber with

good low temperature flexibility.

During this quarterly period, trends indicated by analyses of the above work were investigated.

EXPERIMENTAL PROCEDURE

The experimental procedure followed during this report period was essentially the same as previously described. The use of this technique was continued because it is a convenient method for a rapid evaluation of a variety of candidate systems, since all of the intermediates or components can be processed in the liquid state. Polyol diamine blends containing moisture tend to cause imperfections in the molded parts due to carbon dioxide formed by the water-isocyanate reaction. The polyol-diamine blends were stripped of water by heating them at 120°C for 2 hours under a vacuum of 3 mm Hg.

The polyol-diamine blends were weighed into 16-ounce wide-mouth bottles under anhydrous conditions at room temperature. 0.025 part of stannous octoate catalyst was added to the polyol-diamine blend and the mixture degassed for 15 minutes under a vacuum of 3 mm Hg while mixing with a magnetic stirring bar. A measured amount of tolylene diisocyanate was added to the reaction mixture while agitating under vacuum. Mixing under vacuum was continued for about 30 seconds. The vacuum was then broken and the liquid casting elastomer was poured into molds. The elastomers were cured for 2 hours at 100°C. They were then removed from the molds and post cured 22 hours at 100°C.

The above procedure was modified by elevating the temperature to ca. 60°C when MDI and Teracol 30 were used in the formulation.

A quasi-prepolymer method was developed to handle fast-reacting diisocyanates that are solid at room temperature. A liquid quasi-prepolymer is prepared by reacting the diisocyanate with the polyol for one hour at 80°C at a 4/1

NH₂/OH ratio. The quasi-prepolymer thus may be mixed at room temperature with the polyol-diamine-stannous octoate catalyst blend and cured following the procedure for one shot cast urethane elastomers described above.

RESULTS AND DISCUSSION

Table I lists test data for a series of elastomers based on a 5200 molecular weight polyoxypropylene triol, toluene diisocyanate (TDI), and varying amounts of dichlorobenzidine (DCB) from 1.5/1 to 2.5/1 NH_2/OH ratio.

Table II lists similar data for a series of elastomers based on 7000 molecular weight triol containing large amounts of ethylene oxide, TDI and DCB, varying the NH_2/OH ratio from 1.5/1 to 10/1. The highly hydrophilic 7000 molecular weight triol was used because it was a convenient source of high molecular weight polyether, was compatible at high ratios of amine to hydroxyl, and permitted an investigation of the effect of high ethylene oxide content on the oil resistance.

Figures 1, 2 and 3 illustrate the effect of temperature on the torsional modulus of these elastomers. As the amine to hydroxyl ratio increased, the water and oil swell resistance and the mechanical strength improved, while the torsional modulus at any given temperature increased. However, the slopes of the torsional modulus curves decreased. This means that the torsional modulus was less affected by temperature change at the higher amine to hydroxyl ratios. The high ethylene oxide triol based elastomers had excellent oil swell resistance, but poor moisture absorption.

Table III lists the properties of assorted elastomers including an exploratory effort to investigate use of various polyol bases and combinations. Elastomers PR-1604-C and PR-1605-C investigated the effect of a tertiary amine based triol and tetrol on properties of the resultant elastomer. Elastomers PR-1606-C and PR-1606-N investigated the effects of a 70/30

blend of the polyoxypropylene triol and a 6000 molecular weight ethylene oxide diol. Elastomer PR-1612-H is an elastomer prepared using dianisidine as the diamine. The tertiary amine based elastomers were similar in low temperature torsional modulus to similar polymers made without tertiary amine. This is probably due to the fact that only a small percent of tertiary amine was in these elastomers. The tetrol based elastomer had less desirable low temperature modulus than the triol based one, probably due to the increased cross-linking. The elastomers containing the 6000 molecular weight ethylene oxide diol had improved low temperature modulus when compared to the similar elastomer, PR-1606-D, Table I, that contained no ethylene oxide polymer. The oil absorption was also considerably improved, but at the expense of increased moisture absorption. The improvement in low temperature modulus was probably due to the increased linearity and the higher equivalent weight of the ethylene oxide based polymers. The use of dianisidine as the diamine instead of dichlorobenzidine had an adverse effect on the low temperature torsional modulus, and also increased the room temperature modulus considerably.

Attempts were made to prepare a urethane-urea elastomer from a 3000 molecular weight polyoxypropylene-oxyethylene block polymer containing 40% ethylene oxide, but the material was difficult to process, cracking in the mold. Initial efforts to use p-phenylene diisocyanate in one shot urethane-urea elastomers were unsuccessful due to processing difficulties arising from the high melting point and high reactivity of this material. A quasi-pre-polymer technique using this diisocyanate has largely eliminated these difficulties and will be used to evaluate other diisocyanates.

TABLE I

Effect of NH₂/OH Ratio on Properties of
Experimental Triol 5200-TDI-DCB Elastomers

Pagination No. PR-1606-	D	F	E	J	I
Polyol: Experimental Triol 5200					
Diisocyanate: TDI					
Diamine: DCB					
NH ₂ /OH Ratio	1.5	1.75	2.0	2.25	2.5
<u>Original Properties</u>					
<u>Stress-Strain</u>					
Tensile Strength, psi	1,300	1,480	1,310	1,730	1,200
Ultimate Elongation, %	1,010	680	730	560	760
Modulus, 100%	420	600	590	780	780
300%	680	920	860	1,140	1,160
Hardness, Shore A	78	84	85	88	90
<u>Environmental Properties</u>					
Compression Set, Method B, 70 hrs at 212°F		20.3	25.8	26.5	27.8
ASTM No. 3 Oil, 70 hrs at 212°F					
Wt. Change, %	35.9	30.3	29.0	26.1	24.5
Vol. Change, %	41.7	35.4	33.9	23.1	29.0
Water Absorption, 24 hrs at 75°F, Wt. Change, %	2.3	2.5	2.2	2.1	2.0
Torsional Modulus, G(E=3G)					
-55°C	40,200	51,100	54,500	73,500	69,600
-50°C	18,400	40,300	41,200	43,700	52,800
-45°C	7,500	21,900	10,600	14,100	16,700
Temp. where E = 10,000 psi, °C	-39	-38	-37	-29	> -25

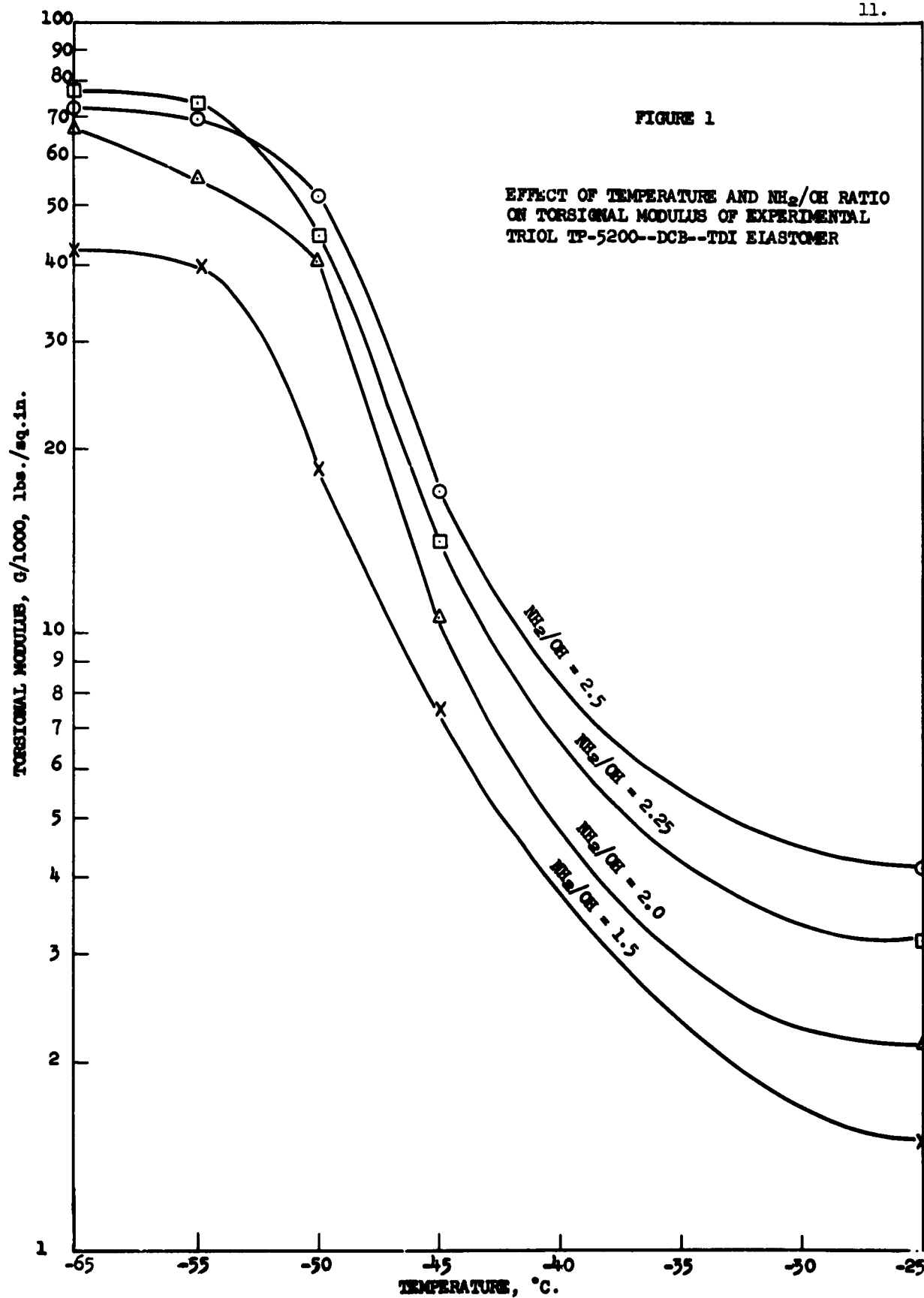
TABLE II

Effect of NH_2/OH Ratio on Properties of
Experimental Triol 7000-TDI-DCB Elastomers

Pagination No. PR-1607-	E	F	K	J	M	P	Q	V	S
Polyol: Experimental Triol 7000 Diisocyanate: Toluene diisocyanate Diamine: Dichlorobenzidine									
NH_2/OH Ratio	1.5	2.0	2.5	3.0	4.0	5.0	6.0	8.0	10.0
Original Properties									
Stress-Strain									
Tensile Strength, psi	260	400	> 730	890	1,560	1,525	1,640	2,330	2,050
Ultimate Elongation, %	1,760	1,810	1,800	1,410	640	430	280	280	280
Modulus, 100%	60	125	220	280	470	635	850	1,300	1,440
300%	90	175	310	410	800	1,200	1,280	1,830	1,790
Hardness, Shore A, Inst	34	48	55	68	72	86	90	97	100
Environmental Properties									
Compression Set, Method B, 70 hrs at 212°F	22.7	32.6	36.9	35.6	57.5	51.3	65.2	78.0	---
ASTM No. 3 Qd1, 70 hrs at 212°F									
Wt. Change, %	9.8	9.6	9.2	8.4	8.2	8.0	7.7	5.9	5.8
Vol. Change, %	11.7	11.7	11.4	11.0	11.0	9.7	9.7	---	8.6
Water Absorption, 24 hrs at 75°F, Wt. Change, %	352	248	193	163	99	104	82	58	44
Torsional Modulus, G(E=30)									
-55°C	31,600	31,500	49,700	55,300	55,100			49,900	
-50°C	15,400	17,500	31,600	37,400	39,800				
-45°C	3,070	5,840	9,930	12,600	34,100			49,900	
25°C	260				885	1,100	1,800	2,200	3,190
Temp. where E = 10,000 psi, °C	- 46	- 43	- 42	- 42					9.

TABLE IIIProperties of Assorted Exploratory One Shot Urethane-Urea Elastomers

<u>Pagination No.</u>	<u>PR-1606-L</u>	<u>PR-1606-N</u>	<u>PR-1612-H</u>
Polyols	Triol 5200 70% Pluracol E-6000 30%		Triol 7000
Diisocyanate	TDI	TDI	TDI
Diamine	DCB	DCB	Dianisidine
NH ₂ /OH Ratio	1.5	2.0	1.5
<u>Original Properties</u>			
<u>Stress-Strain</u>			
Ultimate Strength, psi	752	540	270
Ultimate Elongation, %	160	140	185
Modulus, 100%	485	452	178
Hardness, Shore A	68	75	47
<u>Environmental Properties</u>			
Compression Set, Method B, 70 hrs at 212°F	69	22	
ASTM No. 3 Oil 70 hrs at 212°F			
Wt. Change, %		14.6	9.4
Vol. Change, %			11.1
Water Absorption, 24 hrs at 75°F, Wt. Change, %	18.8	22.8	213.4
<u>Torsional Modulus G(E=3G)</u>			
-55°C	64,000	63,000	64,000
-50°C	11,600	25,000	46,000
-45°C	2,100	7,000	20,000
25°C	540	830	476
Temp. where E = 10,000 psi, °C	- 47	- 42	- 38



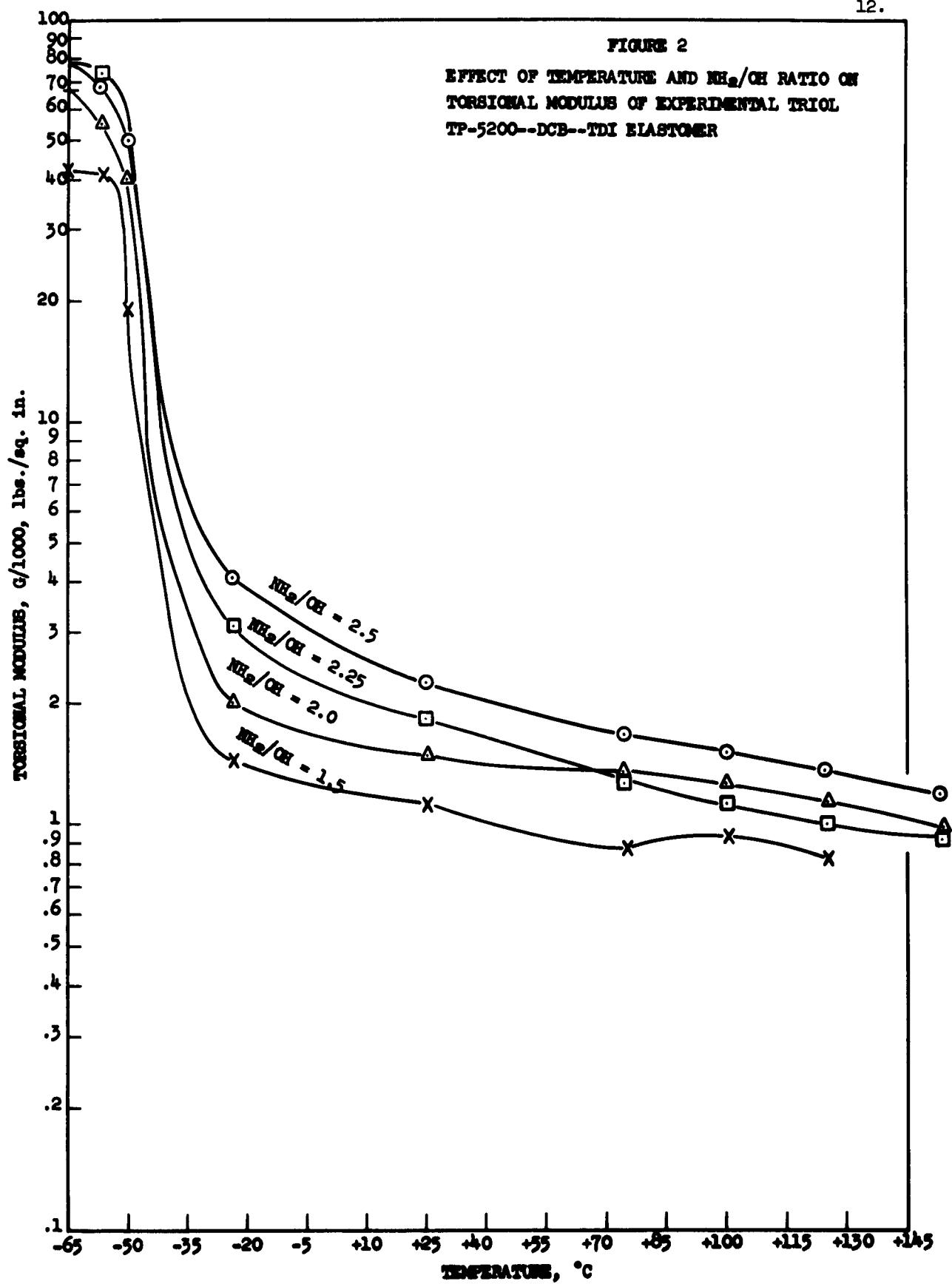
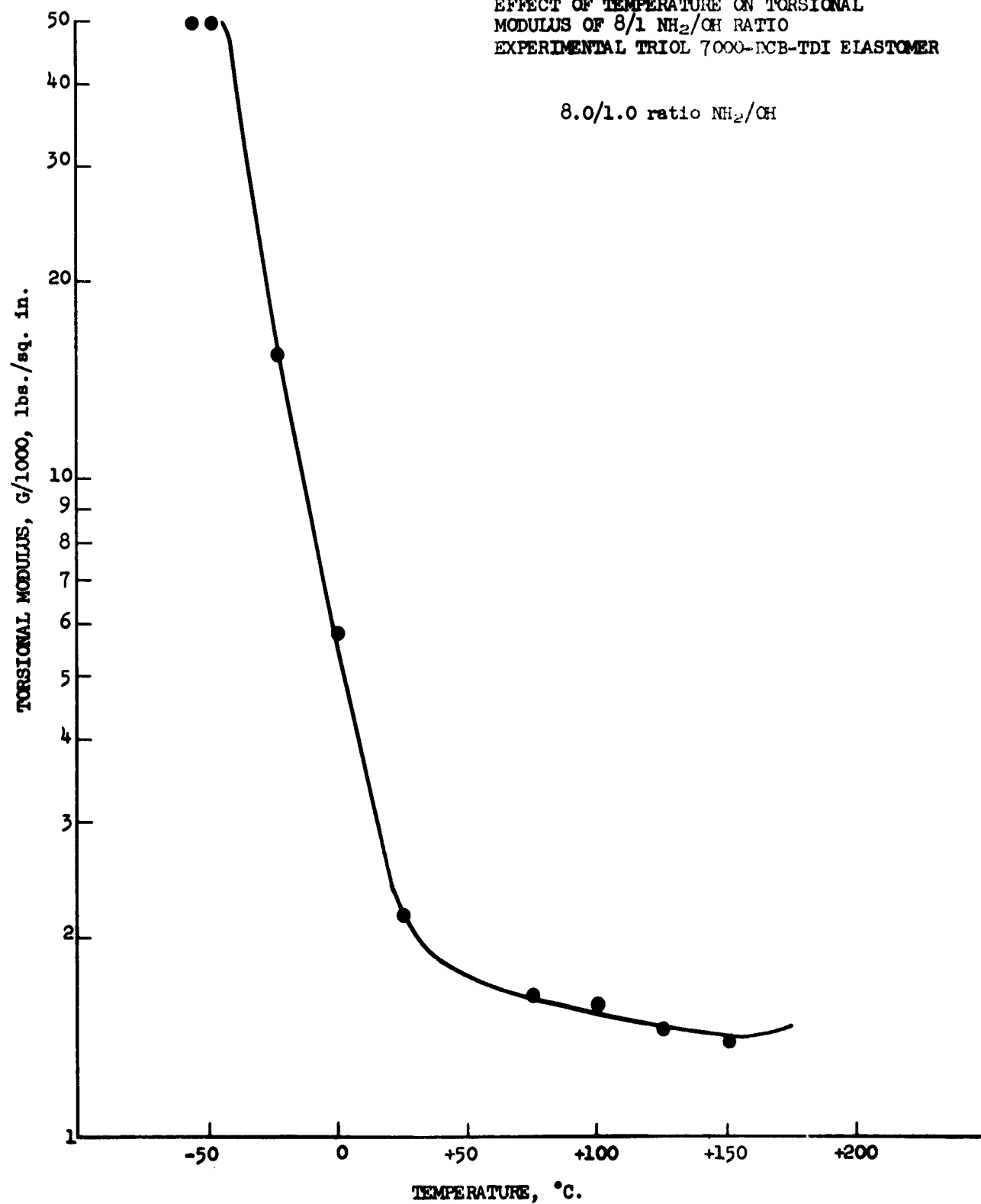


FIGURE 3

EFFECT OF TEMPERATURE ON TORSIONAL
MODULUS OF 8/1 NH_2/OH RATIO
EXPERIMENTAL TRIOL 7000-DCB-TDI ELASTOMER

8.0/1.0 ratio NH_2/OH



FUTURE WORK PROGRAM

A program for next quarter has been outlined below. Although it is anticipated that work in each of the parts listed below will be completed in the third quarter, it is anticipated that additional experimentation along the general lines mentioned in these parts will be continued in the fourth quarter.

Our work has illustrated the major effect of type of diisocyanate and diamine on oil resistance and low temperature flexibility. By variations in the type of each of these variables as listed in Parts I and II, it is to be expected that a characterization of the effect of type of substitution on the aromatic rings and para vs. meta positioning of the functional groups will be accomplished. Also, it is hoped that if any of the diamines containing both amine groups on the same benzene ring are suitable for use in casting urethane elastomers, better low temperature properties will be realized.

Parts III, IV and VI will be run during the remaining two quarters of the contract as suitable materials become available. In Part V it is hoped that by blending polyester in with the polyether polyols, it may be possible to gain oil resistance without adversely affecting the low temperature properties.

I. Other Diisocyanates Using the Quasi-Prepolymer Technique

- A. p-Phenylene diisocyanate
- B. 1,5-Naphthalene diisocyanate
- C. Bitolylene diisocyanate
- D. Dianisidine diisocyanate
- E. Other candidate diisocyanates

II. Other Diamines

- A. p-p'-Diamino-diphenyl sulfone.
- B. p-Phenylene diamines containing negative substitution.
on the benzene ring.
- C. m-Phenylene diamines similar to II-B.
- D. Other candidate diamines.

III. Elastomers Based on Other Heterogeneous High Equivalent Weight
PIURACOLS Containing Assorted Alkylene Oxides.

IV. Elastomers Based on Assorted Alkylene Oxide Block Polymers.

V. Blends of Polyester and Polyether Polyols in Elastomers.

VI. Blends of High Molecular Weight Polyether Polyols and Assorted
Low Molecular Weight Polyols.

APPENDIX I

I. Aromatic Diamines

A. o-Dichlorobenzidine (DCB)

B. Dianisidine

II. Aromatic Diisocyanates

A. Toluene diisocyanate (TDI). 80/20 2,4/2,6-isomer ratio.

B. Para-Phenylene diisocyanate.

III. Catalysts

A. Stannous octoate

IV. Polyols

A. Triol 5200. A 5200 molecular weight polypropylene ether triol.

B. Triol 7000. A 7000 molecular weight polyether triol.

C. PLURACOL E-6000. A 6000 molecular weight ethylene oxide diol.